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Investigation of Advanced Cathode Contacting Solutions in SOFC

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Abstract

Contacting solutions for air electrode in Solid Oxide Cells stacks often implement a ceramic paste made of electronic conducting perovskite, comparable or same as the electro-active material. This contact layer is applied in a green state by wet-powder-spray or screen-printing, and in situ fired during stack commissioning. The low level of necking between ceramic particles causes increased ohmic losses. Moreover the shrinkage usually observed during long term operation in temperature of this layer, due to sintering effect, lead to cracks and contact losses which hinder the cell performance. Increasing cell's footprint, performance and lifetime at the stack level requires appropriate contacting solution.

In this paper we report the investigation of a new advanced monolithic contacting solution, easy to handle, soft and flexible, highly porous and highly conductive. Two different compositions have been investigated, with respect of their compatibility with Crofer (SEM, XRD). In addition, solid oxide cells contacted with this solution as well as with a ceramic paste have also been electrochemically tested up to 1000 hours in order to compare and assess the impact of this contacting solution on cell's performance. Results will be presented and discussed.

Introduction

In SOFC stacks the contacting of the cathode has a significant impact on the resulting power density of the stack. State of the art contacting solutions use green ceramic layers applied by screen-printing or wet powder spraying which are then sintered in-situ during the start-up of the stack. These layers have several drawbacks. Several investigations highlight the challenges of ceramic contact layers [1], [2].
Therefore metallic contact elements were seen as an alternative. Various metal meshes were proposed as a possible means of contacting but some of these which contain noble metals that are rather expensive and other mechanic solutions like S-bend sheet springs are complicated to manufacture and integrate in stacks. Coated meshes of ferritic steels do not possess any flexibility [3].
The reduction of operating temperatures to 750°C and below allows the use cheaper alloys for metallic stack components since there is less strain on those alloys in terms of oxidation. This means on the other hand that in-situ sintering of ceramic contact layers in green state produced by screen-printing or wet powder spraying is growing increasingly difficult. Since the majority of those contact layers are made of cathode material the temperature gap of stack operating temperature and the necessary sintering temperature is growing wider. This leads to a low level of necking between the particles and poor electronic contact.
In most cases the stack seal is composed of somewhat rigid compounds like glass or a reactive braze. The sintering effect occurring during long operation time leads to a shrinkage of the ceramic contact layer with the danger of formation of cracks and loss of contact. Another problem in the mechanical regime comes up with increasing active cell areas and introduction of stamped metal bipolar plates. The range of cell and component tolerances increases and requires some sort of a flexible element to achieve a good contacting.
Therefore the focus of DLR shifted towards flexible metal contact solutions. Metal foams were identified as a promising contact layer. The foams were obtained in two different alloys and two different thicknesses from Alantum/RIST and analyzed with regard to their suitability for contacting SOFCs on the cathode side. Results of the investigations are presented in this paper.

1. Scientific Approach

From the operation conditions of SOFC the main requirements of a contact layer are the following:

- oxidation stability in air up to 900°C
- electronic conductor
- high porosity
- flexibility

Most stack repeat units are not completely flat after integration of the cell but show a certain degree of warp, see figure 1. The trend towards cell areas larger than 100 cm² will even increase warp of SRUs. This may lead to bad contacting in the stack and reduced performance. Also during stack assembly and initial heat up of the stack the material should possess flexibility in order to compensate the tolerances, seal shrinkage and ensure good contact of the whole cell area.

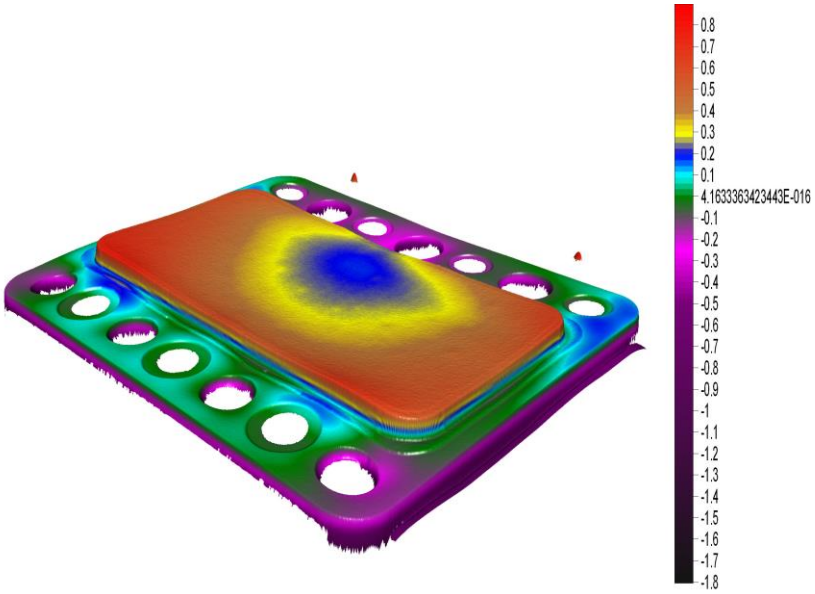

Figure 1: 3D topography of SRU

In order to investigate flexibility the foam was loaded with a defined weight to simulate the contact load of a cell and the resulting thickness was measured. This gives a range within which the foam is able to compensate tolerances of SRUs.

Due to the harsh conditions on the cathode side with its oxidizing atmosphere and high temperature it is important for the material to exhibit a high stability against oxidation by forming a stable oxide scale with good adhesion to the bulk material that prevents any further contact of the metal and the oxygen. Therefore oxidation tests need to be performed. The oxide scale also needs to be an electronic conductor. This can be analyzed by performing XRD on the annealed samples and also electrochemical tests with a cell. The cell tests can be compared to a cell test with the standard ceramic contact layer.

2. Experiments

The contact foams were supplies in two thicknesses for both compounds, see table 1. Since volume is an important issue in stacks only the thinner versions of the foams were used for further analysis. The CuMn-foam is produced from a Cu-foam where Mn-powder is applied. The CoNi-foam is directly made from a CoNi-alloy.

Table 1: Types and characteristics of foams

Foam type	Thickness	Porosity
CuMn	0.371 mm, 1.0 mm	>60%
CoNi	0.434 mm, 1.0 mm	>90%

The deformation test was performed by putting a square 25 cm² sample in a press with mechanical gauges and loading the foam with the equivalent force of 50, 100 and 200

g/cm² which are typical contact weights to be applied to cells and stacks. All experiments were carried out at ambient temperature and with non-oxidized samples. The thickness was measured using thickness gauges on the gap of the press plates. Four measurements were performed at different points of the gap and from the results a mean value was calculated as thickness. This was performed for each of the three loads.

In order to test the oxidation stability the foams were cut into small pieces of 1.5x1.5 cm² and were annealed in air at 900°C for 50 h. Samples were analyzed before and after annealing with XRD and SEM. An EDX mapping is recorded to analyze the distribution of elements and XRD shows which oxides were formed by the alloys during oxidation.

The contact foam also needs to have a high porosity to allow air to pass through to the cathode. The foams have a porosity in the range of 60-90% which is better than most ceramic contact layers. The permeability test is performed according to ISO 4022 which is a standard for porous metal filtration materials and can also be applied for these metal foams. The test measures the differential pressure at a defined fluid flow through a porous sample [4], see figure 2.

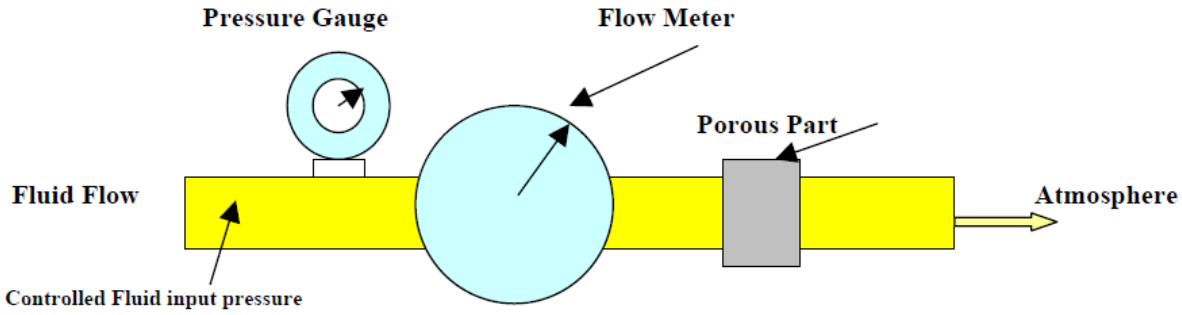

Figure 2: Systematics of permeation test

The equipment was designed and built in-house and incorporates permeation and leak rate measurement positions for substrates, button cells and stack repeat units, see figure 3. The test is performed by forcing nitrogen trough the sample and measuring the differential pressure. The gas flow can be increased in up to 20 steps to a gas flow maximum of 5 slpm and the differential pressure is measured at each point. The volume flow increases every time the differential pressure has stabilized within a certain threshold.

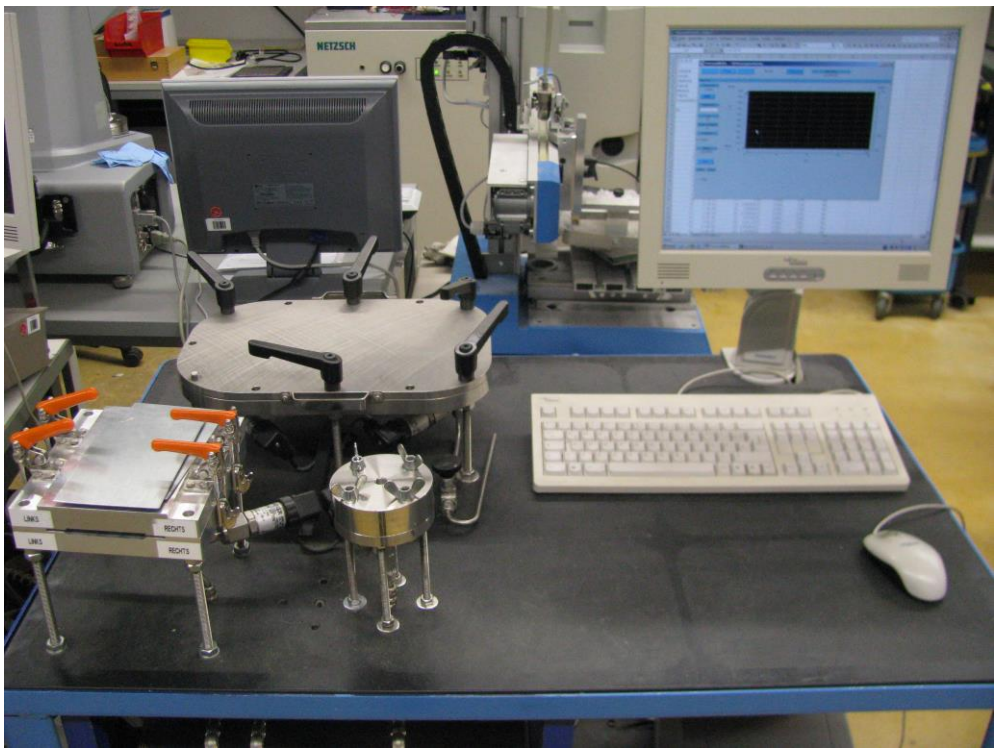

Figure 3: Permeation and leak rate test bench

Electrochemical tests were performed with ASC cells supplied by RIST/South Korea with a square geometry of 50x50 mm and an active area of 16 cm². The cells are standard RIST SOFCs with a NiO/8YSZ cermet anode, an 8YSZ electrolyte, a CGO barrier layer and a LSCF cathode. Testing of the cells was performed using the SOFC test benches at DLR and applying different contact layers to identical ASCs from the same production batch. A weight of 100 g/cm² of active area was applied to the cells. In total three cells were tested, one for each of the different contact layers. Figure 4 shows the schematics of the cell test setup. The metal contact layers were placed on the cathode in non-oxidized state. Application of the LSCF layer was done by screen printing and a platinum mesh was put on while the ceramic was still wet. Afterwards the assembly was dried in air at 60° for 4 h.

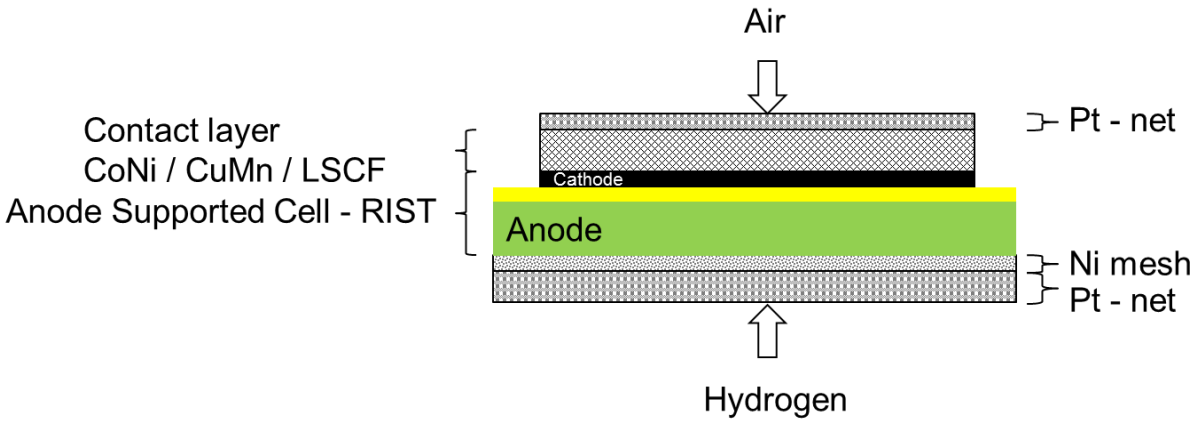

Figure 4: SOFC test setup

Standard tests were performed at 750°C using a gas flow of 1 slpm H_2 on the anode and 2.5 slpm of air on the cathode side. Several gas flow and temperature variations were

done with the working cells. Polarization curves were recorded with a remote controlled Zahner electronic load that integrated in the test bench. Impedance measurements were done with a Zahner IM6 potentiostat/galvanostat frequency analyzer in the range of 0.1 Hz to 100 kHz.

3. Results

Table 2 shows the results for the deformation of the foams under load. At the maximum load of 200 g/cm² both foams deform to about 80% of their original thickness. The behavior with the other loads shows a fairly linear deformation.

Table 2: Thickness of foams under load

Weight [g/cm²]	CoNi foam [µm]	CuMn foam [µm]
0	434	371
50	410	350
100	380	330
200	355	315

The permeability measurement of both metal foams showed really low values for the differential pressure which is due to their high porosity. The resistance to an air gas flow of 5 slpm lead to an increase of 0.2 mbar for the CuMn foam and of 0 mbar for the CoNi foam, see figure 5.

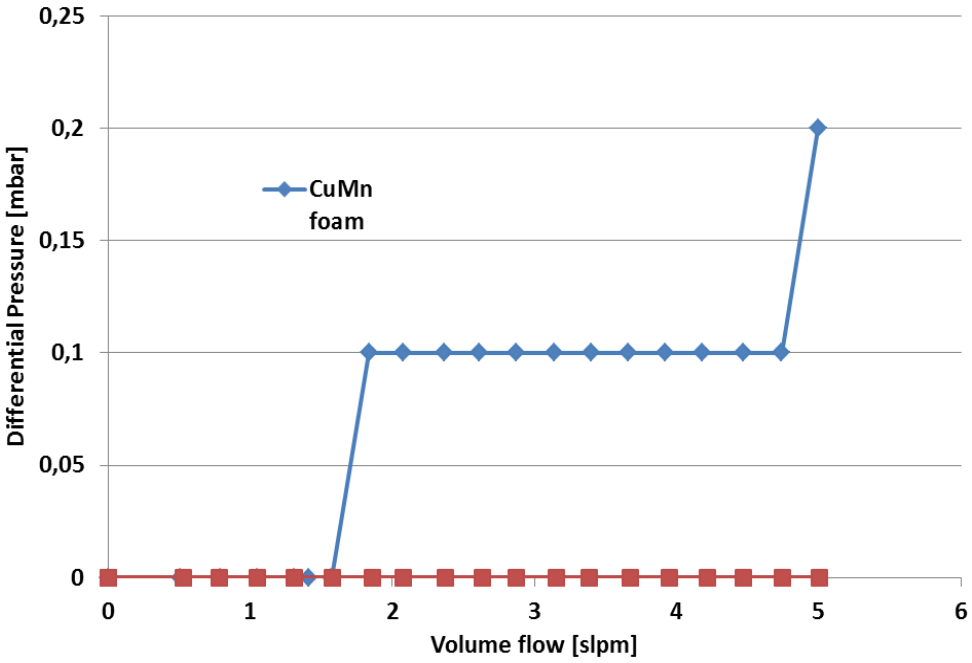

Figure 5: differential pressure of contact foams

Before annealing the foams were analyzed with SEM. The CuMn-foam is a Cu-foam infiltrated with Mn-particles which do not cover the foam structure completely and leaves

large areas of the CuMn-foam uncoated, see figure 6. The CoNi-foam shows a homogeneous distribution of the nickel and the cobalt in the alloy.

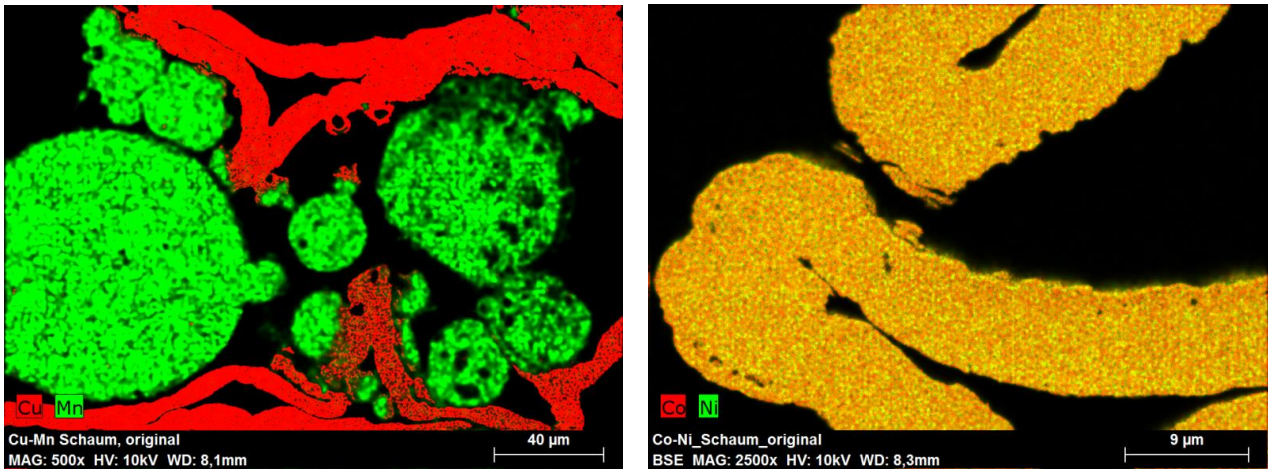

Figure 6: EDX mapping of CuMn-foam (left) and CoNi-foam (right)

Oxidation experiments of the foams showed that the CuMn-foam forms a really thick oxide layer which will likely have a negative impact on electric conductivity and long term stability of the foam, see figure 7. This behavior was expected due to the nature of the foam which consists of two materials rather than a real alloy.

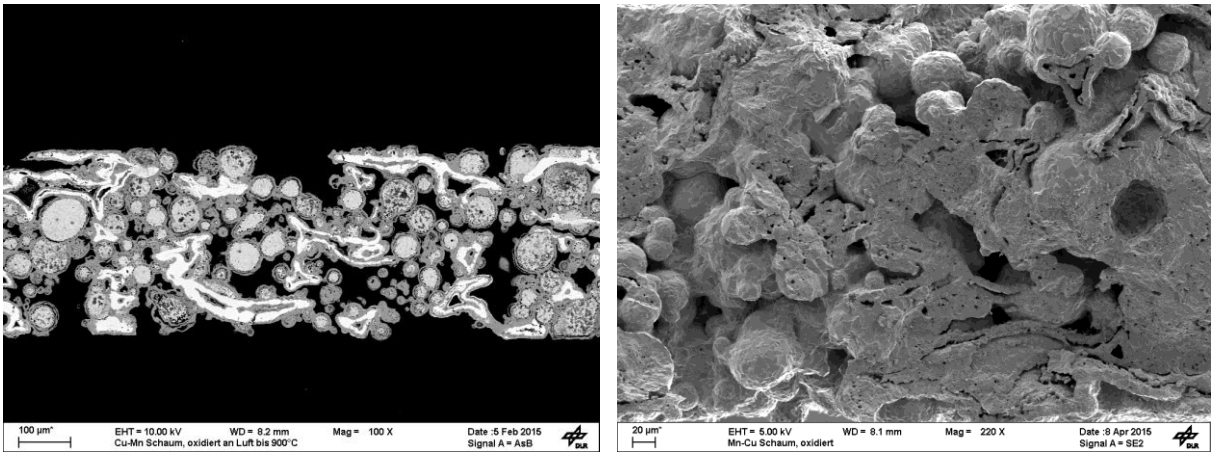

Figure 7: cross section and SEM of CuMn-foam after annealing

Mapping of the elements reveals that oxygen can be detected even deep inside the material which means that the foam is not able to form a protective layer on the surface that is gas-tight and prevents further oxidation of the bulk material. This is also caused by the porous nature of the Mn-particles which allow gas to penetrate deeply into the particles. The CuMn-foam forms Mn-rich oxide scales instead of a spinel phase. The Mn-particles also show some spallation of the oxide scale, see figure 8.

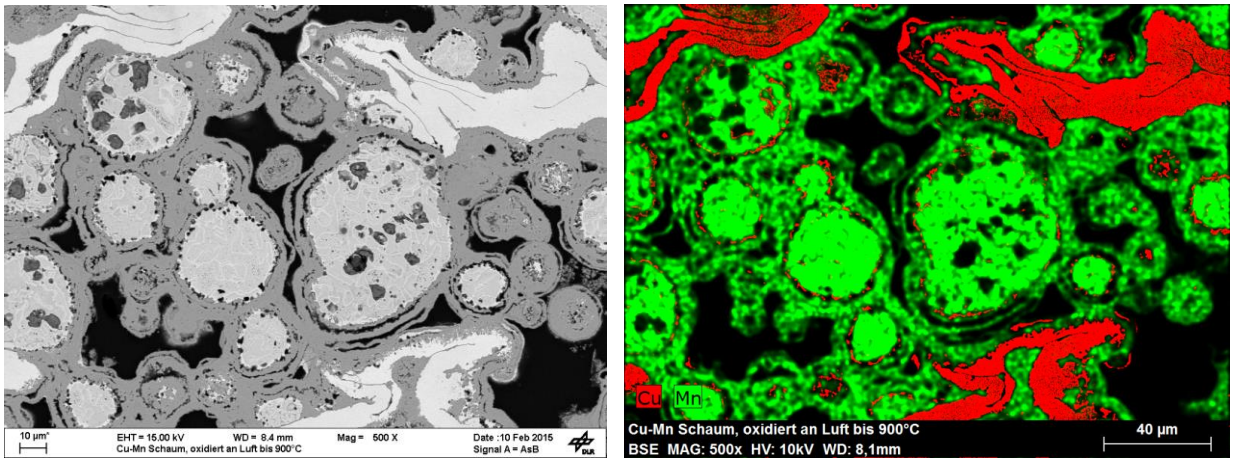

Figure 8: element mapping of CuMn-foam (Cu = red, Mn = green)

The CoNi-foam only forms a thin oxide layer, see figure 9. The oxide scale appears to be dense and covers the whole surface of the foam without visible spallation.

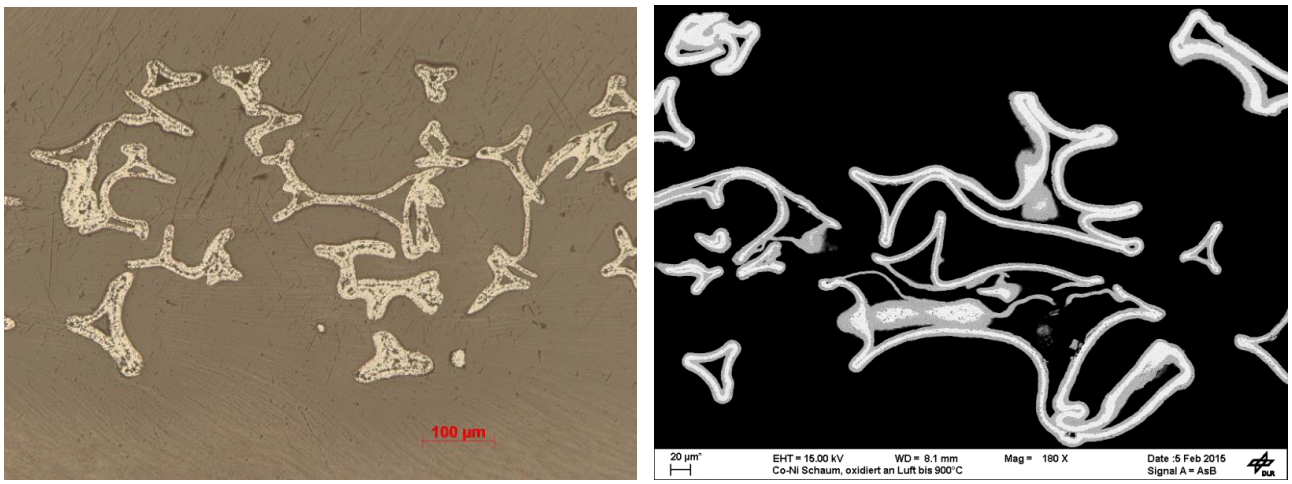

Figure 9: cross section and SEM of CoNi-foam after annealing

Mapping of the elements shows that the oxide scale consists of two layers, see figure 10. A NiO layer is formed directly on the bulk material and on top of the NiO layer a Co_3O_4 scale can be detected. Compared to the non-oxidized foam also some concentration increase of the nickel along grain boundaries in the bulk material was found. Also no spinel phase was detected with XRD for the CoNi-foam, see figure 11.

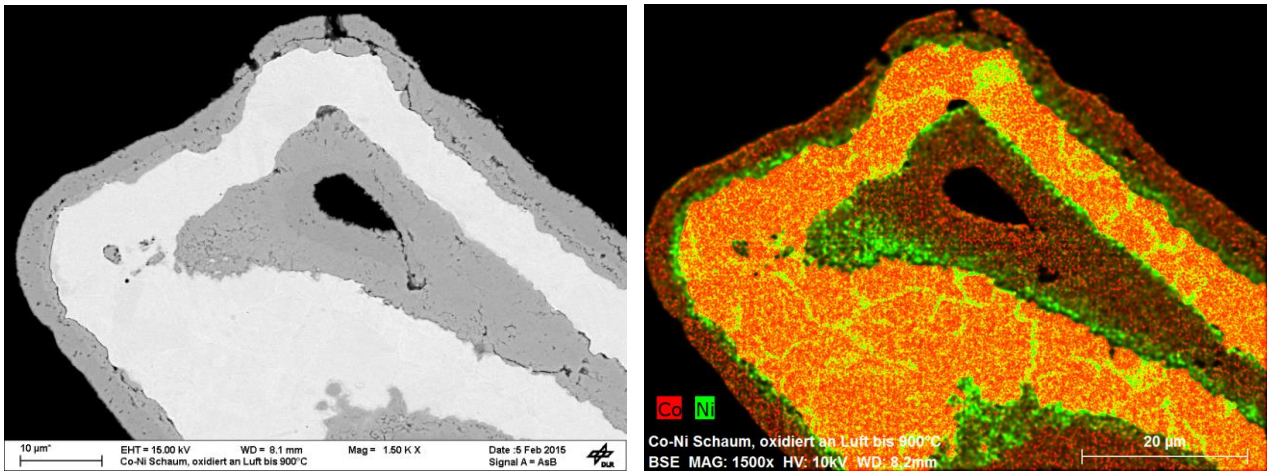

Figure 10: element mapping of CoNi-foam (Co = red, Ni = green)

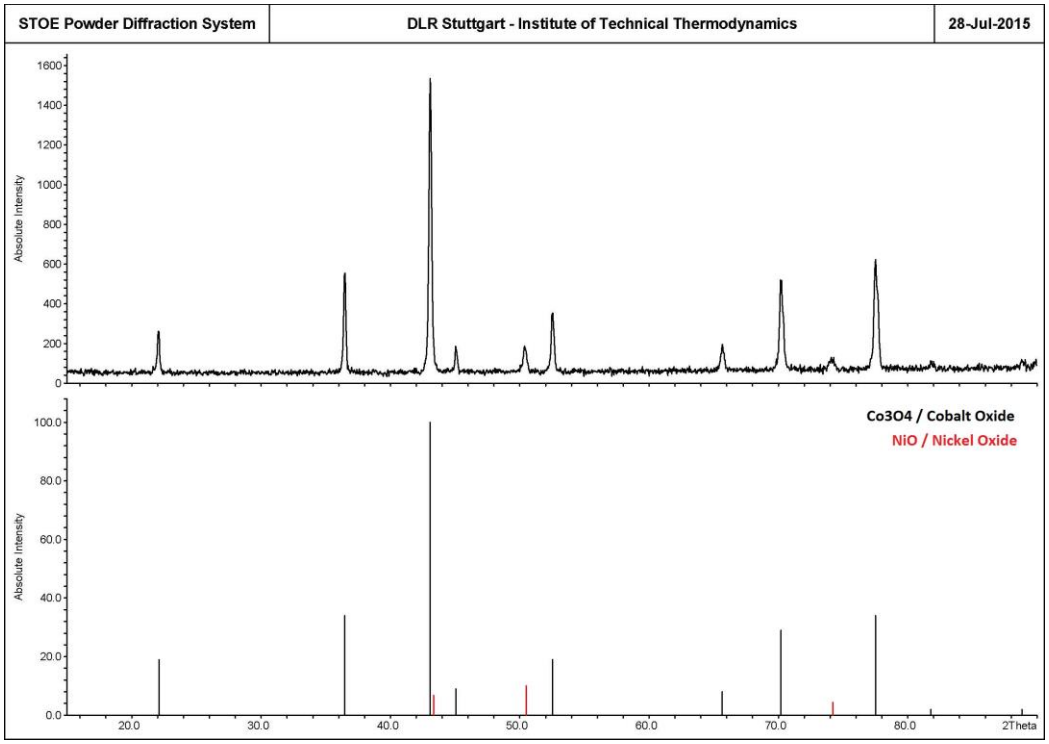

Figure 11: XRD of CoNi foam

Electrochemical measurements of the cells were performed to compare the influence of the contact layer. The first cell was contacted with CuMn-foam. This cell performed poorly, see figure 12. The OCV of this cell was 1122 mV with dry hydrogen and 1052 mV with 3% H_2O. The power density at 0.7 V was recorded at 92 mW/cm². When increasing the load above 153 mA/cm² the cell voltage started to collapse rapidly. After cutting the electronic load off, the cell recovered but this behavior was reproducible. The test was stopped.
The cell with the CoNi-foam yielded a much better power density of 820 mW/cm² at 0.7 V and an OCV of 1175 mV, which is more in line with the values expected of ASCs at this test condition. The standard LSCF and platinum mesh contact layer showed an OCV of 1239 mV and the highest power density of 1037 mW/cm² at 0.768 V. It was not possible to get to 0.7 V in this particular test since the cell performance exceeded the capabilities of the electronic load of the test bench. At high current densities the ohmic resistance in the wiring increases so that the combined voltage of the cell and the auxiliary power supply of the electronic load drops to 0 V and the load can no longer control the current and then

stops increasing the power. In order to compare performances the work point was defined at 0.8 V. Table 3 shows the cell performances of the 3 cells.

Table 3: Power density of the cells at 0.8 V

Cell ID	Contact element	Power density at 0.8 V
RIST ASC_5	CoNi foam	634 mW/cm²
RIST ASC_7	LSCF+Pt mesh	933 mW/cm²
RIST ASC_9	CuMn	80 mW/cm²

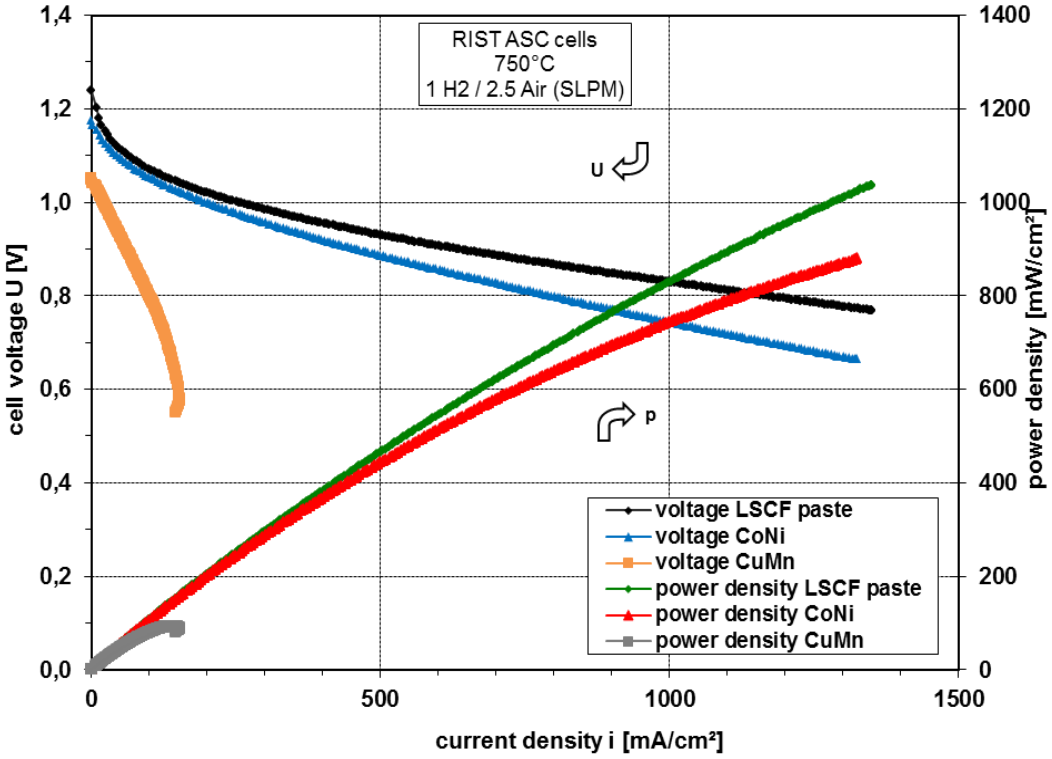

Figure 12: electrochemical performance of ASCs with different contact layers

Impedance measurements were also performed on the cells. This showed a really high R_0 of 108 mΩ for the cell contacted with the CuMn-foam. This is due to the heavy oxidation of this foam. The cell with CoNi-foam is at 10 mΩ and the LSCF+Pt mesh at 6 mΩ, both of which is significantly lower than the value of CuMn, see figure 13.

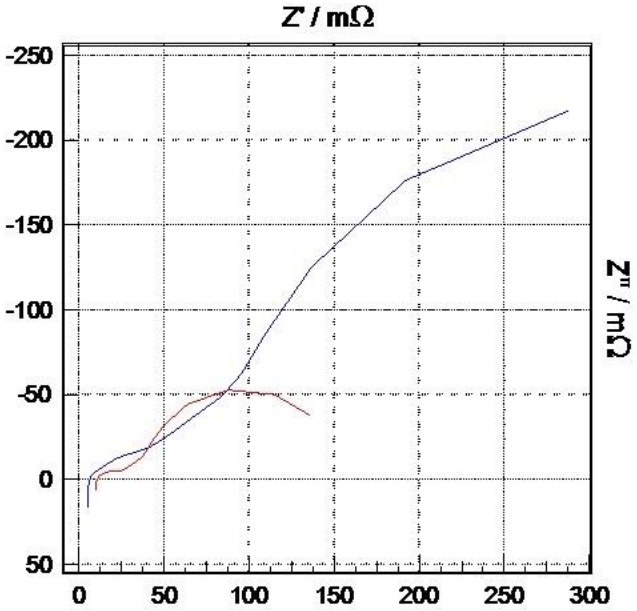

Figure 13: Impedance measurement of Pt mesh (blue) and CoNi foam (red)

Up to now the best performance can still be achieved with the ceramic contact layer. Due to the oxidation problem the CuMn-foam performs badly and is not suitable for SOFC operation in its current specification. The CoNi-foam shows promising results by coming close to power densities which were recorded with the ceramic contact layer.

Both foams do not form a spinel phase in the oxide scale which has a negative impact on long term stability of the foams. A solution would be to find oxidization conditions where the spinel phase is formed and then use pre-oxidized foams. This would increase the life time in SOFC operation. Future work is centered on a long term test to determine and also comparative test with a Crofer 22 contact element to mimic the situation in a stack. Since these were first tests with metal foam contact layers future improvements of setup and the materials will likely bring these materials even closer to the ceramic contact layers and make them an alternative to state-of-the art contact elements.

References

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